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Note

Method of trapping low levels of phosphine at ambient temperature for gas chromatographic analysis

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Hydrogen phosphide, a widely used agricultural fumigant, is toxic at very low concentrations, and hence the health of people that may be exposed to atmospheres containing the gas is of great concern. A threshold limit value–time weighted average (TLV–TWA) of 0.3 ppm for an 8-h work day, 40-h work week has been set by the American Conference of Governmental Industrial Hygienists[1], and this level is believed safe for most working conditions. However, in some fumigation procedures that are currently being practised* exposure of personnel may continue beyond the normal 8-h work day or 40-h work week. In such situations the accepted TLV may not be valid and safety standards may require establishment of a correspondingly lower TLV to avoid hazards[2].

Present methods of detection using glass detector tubes[3] will only allow estimation of phosphine down to 0.1 ppm, but the detection and measurement of considerably lower levels (*e.g.* 0.01 ppm) may be necessary where continuous exposure could occur. Sensitive methods of trapping and analyzing very low levels of phosphine or other volatile compounds in the atmosphere are available[4–7]. However, these require elaborate equipment and procedures designed for laboratory work and are not practical for field use.

A simple practical method for trapping phosphine, a very volatile gas (boiling point −87.4°C), at ambient temperature and analyzing in a GC has been developed and is described here.

MATERIALS AND METHODS

A Bendix 2300 gas chromatograph equipped with alkali flame ionization detector and a nickel column (2 m × 3 mm I.D.) filled Chromosorb 102 (80–100 mesh) was used for the analysis of phosphine. The column temperature was 60°C and the flow-rate of nitrogen carrier gas was 30 ml/min.

Phosphine was generated from Photoxin tablets as previously described[8], and

* Grain cargoes on ships are being fumigated with phosphine and allowed to proceed on voyage with fumigant in the holds, hence personnel on the ships could be exposed to the gas for longer than the normal 8-h working day.

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standards were made by dilution of the gas with air in flasks of 250 ml–10 l. Aliquots of this standard mixture were then injected by a gas-tight syringe into each of three similar nickel tubes (20 cm × 3 mm I.D.) packed with Chromosorb 102 (80–100 mesh), 107 (60–80 mesh) or Tenax GC (35–60 mesh). The tubes had Swagelok fittings at each end with a Swagelok nut and septum at one end for injection of the sample.

The trapping efficiency of the tubes was determined at temperatures of 25, −15 and −78.5°C using sample sizes of 5 to 100 ml. After injection of the phosphine the tubes were then introduced into the modified GC for analysis[4] and the results were calculated with a Hewlett-Packard Model 3380A integrator.

RESULTS AND DISCUSSION

The data for phosphine recovered by the three different adsorbents at −78.5, −15 and 25°C (Table I) show that at the lowest temperature (−78.5°) all of the gas was trapped in all three tubes. At −15°C the tube with Chromosorb 107 gave the best recovery (99%) for a 20-ml sample. The Chromosorb 102 gave 90% and Tenax GC gave 86% recovery. At 25°C Chromosorb 102 was the best with 99% recovery for 5- and 10-ml samples, followed by Chromosorb 107 with 97% for a 5-ml sample and Tenax GC with 70% for a 5-ml sample.

TABLE I

RECOVERY (%) OF 0.4 ng PHOSPHINE IN VARIOUS VOLUMES OF PHOSPHINE–AIR MIXTURE WHEN COLLECTED IN 20 cm × 3 mm I.D. NICKEL TUBES WITH VARIOUS PACKINGS

Packing	*Trapping temperature (°C)*					
	25			*−15*		*−78.5*
	Sample size (ml)			*Sample size (ml)*		*Sample size (ml)*
	5	*10*	*20*	*20*	*30*	*100*
Chromosorb 102	99	99	56	90	86	100
Chromosorb 107	97	90	44	99	89	100
Tenax GC	70	50	18	86	58	100

The above traps were also tested with ten times higher amounts of phosphine, 4 ng instead of 0.4 ng, to determine their absorption capacity, and the results obtained were similar. The data given in Table I were obtained with $1 \cdot 10^{-10}$ A sensitivity and the response was in half scale peak size. This indicates that amounts considerably below the 0.003 ppm could be detected with smaller peaks.

The trapping and analysis of low levels of phosphine at 25°C could be of considerable value in situations where extended exposure to the fumigant might be encountered. For example, in fumigation of ships in transit, where personnel could be continuously exposed to desorbing fumigant and the current threshold limit of 0.3 ppm may be inadequate, an accurate method of detection that can be used under field conditions could be very useful. The described method, which is capable of phosphine analysis down to 0.01 ppm at 25°C, could be applied to such problems, and if greater sensitivity is required it could be achieved by simply lowering the trapping temperature with an ice-salt mixture. For analysis of lower concentrations (at the 0.003 ppm level) dry ice would be required. If samples of the fumigant have to be held for some time before analysis can be made, they should be kept in sampling flasks or in the syringe used to collect the gas; samples of phosphine trapped in the absorbent gradually deteriorate when held for many hours.

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